

Description

Laminated Film for Stretch Packaging

Technical Field

The present invention relates to a laminated film for stretch wrapping suitable for use in wrapping of foods. More particularly, the invention relates to a laminated film for stretch wrapping which is formed of a material without containing either chlorine or a plasticizer for poly(vinyl chloride).

Background Art

Conventionally, foods such as fruits and vegetables, meats, and processed foods placed on lightweight tray are over-wrapped with a stretch wrap film, i.e., pre-packaging, made of poly(vinyl chloride)-based material. Such films have been advantageously employed by virtue of excellent qualities recognized by sellers and consumers. That is, the films maintain the qualities of food products by virtue of the characteristics of film: excellent wrapping properties such as favorable wrapping efficiency and beautiful wrapping finish; excellent elastic recovery, i.e., restoration, from deformation of film induced by, for example, pressing with fingers, after completion of wrapping); excellent bottom sealing property; resistance to detachment from trays during transportation and display; etc.

However, in recent years, hydrogen chloride gas generated from poly(vinyl chloride)-based film during incineration, elution of a large amount of plasticizers contained in poly(vinyl chloride)-based film, and other problems have become critical issues. Thus, materials replacing poly(vinyl chloride)-based film have been studied extensively, and many types of stretch wrap films employing a material, in particular, polyolefin resin, have been proposed. In addition, in recent years extensive studies have been carried out on stretch wrap film having three layers of two components; i.e., both surface layers mainly containing an ethylene-vinyl acetate copolymer, and an intermediate layer mainly containing a polypropylene resin, from the viewpoint of surface characteristics suitable for stretch film, transparency, appropriate heat resistance, freedom in material design, economic merits, etc.

However, at present, currently proposed stretch films formed mainly from polypropylene resin have unsatisfactory wrapping characteristics (for both automated and manual wrapping) such as wrapping efficiency, wrapping finish, elastic recovery, and bottom sealing property, and the overall evaluation of the stretch films on the market, including economic merits, remains unsatisfactory.

The present inventors previously proposed polyolefin-based stretch wrap film having specific viscoelasticity, the film having at least one layer containing a soft polypropylene resin formed from a controlled stereoregularity

based on co-presence of crystalline blocks and amorphous blocks in molecular chains of the resin, and an optional petroleum resin or another polypropylene resin (see, for example, Japanese Patent Application Laid-Open (*kokai*) Nos. 2000-44695 and 2000-44696).

As compared with conventional polyolefin-based stretch wrap films, the films disclosed in Japanese Patent Application Laid-Open (*kokai*) Nos. 2000-44695 and 2000-44696 have excellent characteristics, including wrapping efficiency, wrapping finish, elastic recovery, and bottom sealing property. However, storage stability of feed material pellets (aggregation of feed material pellets during storage, weighing, or transportation) is unsatisfactory, and other properties such as transparency of film and elastic recovery of wrapped film are still inferior to those of poly(vinyl chloride)-based films.

Meanwhile, a wrap film composed of a soft polypropylene resin having a specific stereoregularity and produced in the presence of a metallocene catalyst, and an olefin polymer is disclosed (see, for example, Japanese Patent Application Laid-Open (*kokai*) No. 2002-47383).

The film disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 2002-47383 exhibits relatively favorable stretch wrap film characteristics in terms of, for example, transparency and elastic recovery. However, since restoration behavior of the film being stretched is instantaneous, when wrapping is carried out by the use of an

automatic wrapping machine, the stretched film happens to be undesirably restored during a very short period of folding the film under the bottom of a tray. Thus, the insufficiently stretched film tends to generate wrinkles and have a poor cut property.

#### Disclosure of the Invention

An object of the present invention is to provide a chlorine-free stretch film which is excellent in terms of storage stability of feed material pellets, wrapping efficiency, wrapping finish, elastic recovery, bottom sealing property, transparency, etc. and has favorable long-term stability and economic merits.

The present inventors have carried out extensive studies so as to attain the aforementioned object, and have found that a laminated film comprising at least three layers including an intermediate layer formed of a resin layer containing a specific polypropylene resin having controlled stereoregularity, a crystalline polypropylene resin, and a petroleum resin, and two surface layers containing, as a main component, an ethylene polymer successfully provides a chlorine-free stretch film which has excellent characteristics such as wrapping efficiency, wrapping finish, elastic recovery, bottom sealing property, and transparency, and has favorable long-term stability and economic merits as well. The present invention has been accomplished on the basis of this finding.

Accordingly, the present invention provides a laminated film for stretch wrapping which comprises at least three layers, characterized in that the laminated film has both surface layers comprising, as a main component, component (A) which is an ethylene polymer, and has at least one intermediate layer formed of a mixed resin layer comprising, as a main component, a resin composition containing the following component (B) in an amount of 30 to 75 % by weight: a polypropylene resin having controlled stereoregularity satisfying the following requirements (1) and (2):

(1) a meso pentad fraction [mmmm] as determined from a  $^{13}\text{C}$ -NMR spectrum is 0.2 to 0.7, and

(2) a racemic pentad fraction [rrrr] and (1-mmmm) satisfy the following relation:

$$[\text{rrrr}/(1-\text{mmmm})] \leq 0.1;$$

the following component (C) in an amount of 20 to 60 % by weight:

a crystalline polypropylene resin having a crystal melting peak temperature of 120°C or higher; and

the following component (D) in an amount of 5 to 30 % by weight:

at least one resin selected from among petroleum resin, terpene resin, coumarone-indene resin, rosin resin, and hydrogenated derivatives thereof.

The term "main component" in this description is defined as the component occupying in excess of 50 % by weight.

### Best Modes for Carrying Out the Invention

The present invention will next be described in detail.

The laminated film for stretch wrapping of the present invention has at least three layers including two surface layers and at least one intermediate layer.

Examples of the ethylene polymer (A) serving as a main component of the aforementioned surface layers include low-density polyethylene, linear low-density polyethylene, linear ultra-low-density polyethylene, medium-density polyethylene, high-density polyethylene, and copolymers formed from ethylene serving as a main component. Specific examples of the copolymers include a copolymer or a polygeneric copolymer of ethylene and one or more comonomers and a mixture composition thereof. Examples of the comonomers include C<sub>3</sub> to C<sub>10</sub>  $\alpha$ -olefins such as propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, heptene-1, and octene-1; vinyl esters such as vinyl acetate, and vinyl propionate; unsaturated carboxylate esters such as methyl acrylate, ethyl acrylate, methyl methacrylate, and ethyl methacrylate; ionomers thereof; and unsaturated compounds such as conjugated dienes and non-conjugated dienes. The ethylene polymer generally has ethylene unit content greater than 50 % by weight. As used herein to modify the comonomer, the notation "C<sub>x</sub> to C<sub>y</sub>", wherein x and y are each integers, means that the comonomer contains from x carbon atoms to y carbon atoms per comonomer.

Among the above ethylene polymers (A), preferred is at least one ethylene polymer selected from among low-density polyethylene, linear low-density polyethylene, linear ultra-low-density polyethylene, ethylene-vinyl acetate copolymer, ethylene-acrylate ester copolymer, and ethylene-methacrylate ester copolymer. Examples of the acrylate ester include methyl acrylate and ethyl acrylate, and examples of the methacrylate ester include methyl methacrylate and ethyl methacrylate.

Among the aforementioned ethylene polymers (A), an ethylene-vinyl acetate copolymer which has a vinyl acetate unit content of 5 to 25 % by weight and a melt flow rate (JIS K 7210, 190°C, under a load of 21.18 N) of 0.2 to 10 g/10 minutes is most preferred.

When the vinyl acetate unit content is less than 5 % by weight, the produced film may have high hardness and reduced flexibility and elastic recovery. In this case, surface tackiness is difficult to reveal. When the vinyl acetate content is in excess of 25 % by weight, the film has excessive surface tackiness, and unwinding characteristic and appearance of the film tend to be impaired. When the melt flow rate is less than 0.2 g/10 minutes, extruding ability may be reduced, whereas when the melt flow rate is in excess of 10 g/10 minutes, reliable film formation cannot be performed, and unevenness in film thickness, decrease and fluctuation in mechanical strength, and similar phenomena are prone to occur, which are not preferred.

No particular limitation is imposed on the method for producing the aforementioned ethylene polymers (A), and any known polymerization methods employing a known olefin polymerization catalyst may be employed. Examples of the polymerization method include slurry polymerization, solution polymerization, bulk polymerization, gas phase polymerization which employ a multi-site catalyst represented by Ziegler-Natta catalyst or a single-site catalyst represented by a metallocene catalyst, and bulk polymerization employing a radical initiator.

To the aforementioned ethylene polymers (A) forming the surface layers, additives such as an anti-oxidant, an anti-clouding agent, an antistatic agent, a lubricant, and a nucleating agent may be added in accordance with needs.

The intermediate layer of the laminated film of the present invention, which is composed of at least one intermediate layer provided between the two surface layers, is formed of a mixed resin layer comprising, as a main component, a resin composition containing the following component (B), component (C), and component (D):

component (B): a polypropylene resin having controlled stereoregularity satisfying the following requirements (1) and (2):

(1) a meso pentad fraction [mmmm] as determined from a  $^{13}\text{C}$ -NMR spectrum is 0.2 to 0.7, and

(2) a racemic pentad fraction [rrrr] and (1-mmmm) satisfy the following relation:



$[rrrr/(1-mmmm)] \leq 0.1;$

component (C): a crystalline polypropylene resin having a crystal melting peak temperature of 120°C or higher; and

component (D): at least one resin selected from among petroleum resin, terpene resin, coumarone-indene resin, rosin resin, and hydrogenated derivatives thereof.

No particular limitation is imposed on the polypropylene resin having controlled stereoregularity serving as component (B), so long as the resin satisfies the aforementioned requirements. The meso pentad fraction  $[mmmm]$  is preferably 0.3 to 0.6. The ratio of the racemic pentad fraction  $[rrrr]$  to  $(1-mmmm)$  is preferably  $[rrrr/(1-mmmm)] \leq 0.08$ , more preferably  $[rrrr/(1-mmmm)] \leq 0.06$ , particularly preferably  $[rrrr/(1-mmmm)] \leq 0.05$ .

When the meso pentad fraction  $[mmmm]$  of the polypropylene resin having controlled stereoregularity serving as component (B) is (1) in excess of 0.7, flexibility is reduced. Thus, a film formed from the composition is difficult to satisfy characteristics required for serving as a stretch wrap film such as wrapping efficiency, wrapping finish, elastic recovery, and bottom sealing property. When the meso pentad fraction  $[mmmm]$  is (1) less than 0.2, crystallinity is excessively lowered, thereby readily forming aggregation of feed material pellets and lowering film forming-ability. When the ratio of the racemic pentad fraction  $[rrrr]$  to  $(1-mmmm)$ ,  $[rrrr/(1-mmmm)]$  is (2) in excess of 0.1, feed material pellets may become sticky and may be

aggregated during storage.

The meso pentad fraction [mmmm], which characterizes the polypropylene resin having controlled stereoregularity serving as component (B) employed in the present invention, refers to a meso fraction in terms of pentad unit contained in a polypropylene molecule chain, the meso fraction being determined from signals attributed to a methyl group in a  $^{13}\text{C}$ -NMR spectrum in accordance with a method proposed by A. Zambelli et al. (Macromolecules, 6, 925(1973)). The greater the meso pentad fraction, the higher the stereoregularity of the polypropylene resin.

Similarly, the racemic pentad fraction [rrrr] refers to a racemic fraction in terms of pentad unit contained in a polypropylene molecule chain. The ratio  $[\text{rrrr}/(1-\text{mmmm})]$  is obtained from the aforementioned pentad-unit-basis meso fraction and racemic fraction, and serves as an index for showing uniformity in stereoregularity distribution of the propylene polymer. The greater the ratio, the wider the distribution profile of stereoregularity. In this case, similar to the case where conventional polypropylene is produced in the presence of a known catalyst system, a mixture of high-stereoregularity polypropylene (PP) and amorphous polypropylene (APP) is produced. As a result, film forming-ability is lowered due to increase in stickiness, and the resultant film exhibit poor transparency.

No particular limitation is imposed on the polypropylene resin having controlled stereoregularity

serving as component (B) employed in the present invention, so long as the resin satisfies the aforementioned specific requirements (1) and (2). The polypropylene resin may be a copolymer with a comonomer (2 % by weight or less) other than propylene. Examples of the comonomer include ethylene, 1-butene, 1-pentene, 4-methyl-pentene-1, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene. The propylene polymer may be a copolymer obtained through copolymerization of propylene with one or more these comonomers.

The aforementioned polypropylene resin having controlled stereoregularity may be used singly or in combination of two or more species. Generally, such polypropylene resins having a melt flow rate (MFR) (JIS K 7210, 230°C, under a load of 21.18 N) of 0.4 to 20 g/10 minutes, preferably 0.5 to 10 g/10 minutes are employed.

No particular limitation is imposed on the method for producing the polypropylene resin having controlled stereoregularity serving as component (B) employed in the present invention, and any method may be employed so long as the aforementioned requirements (1) and (2) are satisfied. For example, the polypropylene resin is produced preferably through a known method (see WO 99/67303) including (co)polymerization of propylene in the presence of a metallocene catalyst formed from a transition metal compound having a cross-linking structure by the mediation of two cross-linking groups and, in combination, a cocatalyst.

The crystalline polypropylene resin serving as component (C) has a crystal melting peak temperature of 120°C or higher, preferably 130°C to 165°C. When ethylene polymer (A) is employed as a main component in both surface layers and the crystalline polypropylene resin having a crystal melting peak temperature of 120°C or higher is incorporated into the intermediate layer, the heat sealing temperature range can be sifted to higher temperature. When the crystal melting peak temperature is lower than 120°C, the heat sealing temperature range becomes narrower, resulting in difficulty in reliable and sufficient heat sealing. The crystal melting peak temperature of the entire intermediate layer, as determined by the use of a differential scanning calorimeter, is preferably higher than that of the surface layers, by 20°C or more, more preferably 30°C or more, particularly preferably 50°C or more. When the difference in crystal melting peak temperature between the surface layers and the intermediate layer is less than 20°C, heat sealing temperature range becomes narrow, failing to attain heat employable heat sealing characteristics and readily forming holes in the film during heat sealing.

Examples of the crystalline polypropylene resin having a crystal melting peak temperature of 120°C or higher include propylene homopolymer and random copolymers and block copolymers of propylene and another polymerizable monomer. No particular limitation is imposed on the stereostructure of these propylene resins, and propylene polymers of isotactic

structure, atactic structure, syndiotactic structure, or mixed structure thereof may be employed. Examples of the copolymerizable monomer include C<sub>4</sub> to C<sub>12</sub>  $\alpha$ -olefins such as ethylene, 1-butene, 1-hexene, 4-methylpentene-1, and 1-octene; and dienes such as divinylbenzene, 1,4-cyclohexadiene, dicyclopentadiene, cyclooctadiene, and ethylidenenorbornene. These monomers may be copolymerized two or more species in combination. Among these, ethylene is preferred in the present invention. Examples of random copolymers include propylene-ethylene random copolymer and propylene-ethylene-butene-1 copolymer. Examples of block copolymers include propylene-ethylene block copolymer and reactor-type polypropylene elastomer. Specific examples of commercial products thereof include IDEMITSU TPO (product of Idemitsu Petrochemical Co., Ltd.), P.E.R. (product of Tokuyama Corporation), NEWCON (product of Chisso Corporation), Catalloy (Adsyl, Adflex) (product of Montell SDK Sunrise Ltd.), EXCELLEN EPX (product of Sumitomo Chemical Co., Ltd), and Zelas (product of Mitsubishi Chemical Corporation).

Of these, propylene-ethylene random copolymer and propylene-ethylene-butene-1 copolymer are preferably employed from the viewpoint of transparency, heat resistance, cost, etc., while reactor-type polypropylene elastomer is preferably employed from the viewpoint of improvement of low-temperature characteristics, softness, transparency, etc.

These crystalline polypropylene resins may be used singly or in combination of two or more species. Generally,

such polypropylene resins having a melt flow rate (MFR) (JIS K 7210, 230°C, under a load of 21.18 N) of 0.4 to 20 g/10 minutes, preferably 0.5 to 10 g/10 minutes are employed.

Component (D) is at least one resin (hereinafter may be referred to as "petroleum resin") selected from among petroleum resin, terpene resin, coumarone-indene resin, rosin resin, and hydrogenated derivatives thereof. Such component (D) is effectively used for the purpose of further enhancement of wrapping characteristics such as film firmness, cut property, and performance of folding stability of the bottom as well as transparency. Examples of the petroleum resin include alicyclic petroleum resins obtained from cyclopentadiene or its dimer, aromatic petroleum resins obtained from a C9 fraction, and alicyclic-aromatic copolymerized petroleum resin. Examples of the terpene resin include terpene resin and terpene-phenol resin which are derived from  $\beta$ -pinene. Examples of the rosin resin include rosin resins such as gum rosin and wood rosin and esterified rosin resins such as those esterified with glycerin, pentaerythritol, etc. Among the aforementioned petroleum resins, hydrogenated derivatives are preferred from the viewpoint of color tone, thermal stability, and miscibility. Petroleum resins having a variety of softening points are produced mainly depending on the molecular weight thereof. Among them, petroleum resins having a softening point of 100 to 150°C, preferably 110 to 140°C are preferably employed. Specific examples of commercial products thereof include

PETROSIN and Hi-rez (products of Mitsui Chemicals, Inc.), Arkon (product of Arakawa Chemical Industries, Ltd.), Clearon (product of YASUHARA CHEMICAL Co., Ltd.), I-MARV (product of Idemitsu Petrochemical Co., Ltd.), and Escorez (product of Tonex Co., Ltd.).

The mixed resin layer serving as an intermediate layer mainly comprises the aforementioned resin composition containing component (B) in an amount of 30 to 75 % by weight (preferably 40 to 65 % by weight), component (C) in an amount of 20 to 60 % by weight (preferably 25 to 50 % by weight), and component (D) in an amount of 5 to 30 % by weight (preferably 10 to 20 % by weight).

When the component (B) content is less than 30 % by weight or the component (C) content is in excess of 60 % by weight, characteristics of the polypropylene resin of the present invention having controlled stereoregularity cannot be fully attained, and elastic recovery and flexibility of the produced film tends to decrease. When the component (B) content is in excess of 75 % by weight or the component (C) content is less than 20 % by weight, the produced film has excessive flexibility (i.e., less firmness) resulting in impaired cut property, poor heat resistance, thereby failing to fully attain practical heat sealability. When the component (D) (petroleum resin) content is in excess of 30 % by weight, mechanical strength and low-temperature characteristics are impaired. In this case, there arise problems such as tearing of the produced film, and bleeding

of petroleum resin on a film surface as time elapsed, resulting in adhesion between each other in film roll products. When the component (D) content is less than 5 % by weight, restoration behavior of the produced film against elongation is instantaneous. Thus, the elongated film happens to be undesirably restored during a very short period of folding the film under the bottom of a tray, when wrapping is carried out by the use of an automatic wrapping machine. Therefore, the component (D) (petroleum resin) content is preferably 10 to 20 % by weight.

The laminated film for stretch wrapping of the present invention includes at least three layers: i.e., (H)/(M)/(H), wherein (H) denotes a surface layer and (M) denotes an intermediate layer. The laminated film may have two or more intermediate layers in accordance with, for example, uses and purposes. For example, the laminated film may have a layer structure (H)/(M1)/(M2)/(H).

Preferably, the entirety of the laminated film for stretch wrapping of the present invention has a storage modulus ( $E'$ ) of  $5.0 \times 10^7$  Pa to  $5.0 \times 10^8$  Pa as determined through dynamic viscoelasticity measurement with the frequency of 10 Hz and at the temperature of 20°C, and has a loss tangent ( $\tan\delta$ ) within a range of 0.2 to 0.8.

The loss tangent ( $\tan\delta$ ) is a ratio of loss modulus ( $E''$ ) to storage modulus ( $E'$ ); i.e.,  $\tan\delta = E''/E'$ . When a film is present within a temperature range where loss tangent is large, loss modulus ( $E''$ ) of the material (i.e., viscosity-



related property) is significant among viscoelasticity. Therefore, stress relaxation or similar phenomena of the stretch film during wrapping steps (e.g., manual wrapping and wrapping by the use of an automated machine) can be evaluated through employment, as reliable indices, of  $\tan\delta$  values and a temperature range where  $\tan\delta$  is large.

When the storage modulus ( $E'$ ) is less than  $5.0 \times 10^7$  Pa, the film has excessive flexibility that induces small stress against deformation, resulting in unfavorable operability, poor powerfulness of the film of packaged products. Such a film is not suited for stretch film. On the contrary, when the storage modulus ( $E'$ ) is in excess of  $5.0 \times 10^8$  Pa, the film is less stretchable due to high hardness, resulting in deformation or rupture of trays. Therefore,  $E'$  preferably falls within a range of  $8.0 \times 10^7$  Pa to  $3.0 \times 10^8$  Pa. When  $\tan\delta$  is less than 0.2, restoration behavior of the produced film is instantaneous. Thus, the elongated film happens to be undesirably restored during a very short period of folding the film under the bottom of a tray resulting in poor powerfulness of the film and in generation of wrinkles. In addition, thermal melt adhesion of the film during stretch wrapping cannot be sufficiently performed, leading to poor heat-seal conditions of the bottom of trays; i.e., the film at the bottom of packaged products is readily detached during the course of transportation and display. Further, when  $\tan\delta$  is in excess of 0.8, the film exhibits elastic deformation, although good wrapping finish is attained. Thus, the film of

packaged products has weak tension against outer force, and the film on the upper side of trays is readily slackened through stacking of the packaged products during transportation and display, leading to decrease in quality of the products. In the case of automated wrapping, such film readily causes problems such as chuck failure, since the film is well elongated in the machine direction. The  $\tan\delta$  falls particularly preferably within a range of 0.30 to 0.60.

In addition to the intermediate layer, another layer (S layer); e.g., a recycle resin layer, as well as another thermoplastic layer; e.g., a polyamide resin layer, an ethylene-vinyl alcohol copolymer layer, or a polyester layer, for imparting the film with gas barrier property may be inserted between surface layers to form a laminated film, so long as the object of the present invention is not impaired. Furthermore, in order to enhance interlayer adhesion, an adhesive or an adhesive resin layer may also be inserted between the layers to form a laminated film.

When the film for stretch wrapping of the present invention has a layer structure including two or more (H) layers, (M) layers, (S) layers, and other layers, in each layer species, the resin composition and other properties may be different from layer to layer or common to all the layers.

The film of the present invention generally has a thickness falling within a range which is generally employed with respect to film for stretch wrapping; i.e., about 8 to 30  $\mu\text{m}$ , typically 10 to 20  $\mu\text{m}$ . The ratio of the thickness of

the aforementioned mixed resin layer included in the laminated film of the present invention to the total laminated film thickness is generally 0.2 to 0.9, preferably 0.3 to 0.8. Specifically, the mixed resin layer preferably has a thickness of 5 to 20  $\mu\text{m}$  from the viewpoint of cost and characteristics required for stretch wrap film.

The film of the present invention may be produced through melt extrusion of material by the use of an extruder and film formation (i.e., inflation molding or T-die molding). The laminated film is advantageously formed through co-extrusion by means of a plurality of extruders with multilayer dies. From a practical viewpoint, a resin material is preferably inflation-molded through melt-extruding via ring dies. The blow-up ratio (bubble diameter/die diameter) is preferably 4 or more, particularly preferably 5 to 7. The molded film may be cooled outside the tube or outside and inside the tube. The thus-formed film may be heated at a temperature equal to or lower than the crystallization temperature of the resin and stretched about 1.2 to 5 folds in the machine direction of the film or biaxially stretched about 1.2 to 5 folds in the machine and transverse direction of the film on the basis of the difference in stretch speed between nip rollers. Through the aforementioned treatments, the film can be imparted with improved cut property and heat shrinking property.

To the surface layers and/or mixed resin layer of the film of the present invention, a recycle resin obtained from

trimming wastes or other sources or the following additives for imparting the film with properties such as anti-clouding, antistatic, lubricating, and self-adhesion properties may be appropriately incorporated, without deviating from the scope of the present invention.

Examples of the additives include aliphatic alcohol fatty acid esters obtained as a compound of a C1 to C12, preferably C1 to C6 aliphatic alcohol and a C10 to C22, preferably C12 to C18 fatty acid, polyalkylene ether polyols, and paraffin oils. Specific examples of the esters include monoglycerin oleate, polyglycerin oleate, glycerin triricinoleate, glycerin acetylricinoleate, polyglycerin stearate, polyglycerin laurate, methyl acetylricinoleate, ethyl acetylricinoleate, butyl acetylricinoleate, propylene glycol oleate, propylene glycol laurate, pentaerythritol oleate, polyethylene glycol oleate, polypropylene glycol oleate, sorbitan oleate, sorbitan laurate, polyethylene glycol sorbitan oleate, and polyethylene glycol sorbitan laurate. Examples of the ether polyols include polyethylene glycol and polypropylene glycol. At least one species of these compounds is preferably added in an amount of 0.1 to 12 parts by weight, more preferably 1 to 8 parts by weight, to 100 parts by weight of a resin component forming each layer.

#### Examples

The present invention will next be described in more detail by way of examples, which should not be construed as

limiting the invention thereto. Determination of physical properties and evaluation of the films and the materials for forming the films described in the specification were carried out through the following methods. In the specification, the direction of film extrusion from an extruder is referred to as the "machine direction," and the direction normal to the machine direction is referred to as the "transverse direction."

(1) Meso pentad fraction [mmmm] and racemic pentad fraction [rrrr]

The fractions were determined by the use of JNM-GSX-270 (product of JEOL Ltd.,  $^{13}\text{C}$ -nuclear magnetic resonance frequency: 67.8 MHz) under the following conditions.

Mode:  $^1\text{H}$  complete decoupling

Pulse width: 8.6  $\mu\text{seconds}$

Pulse interval: 30 seconds

Integration: 7,200 times

Solvent: a mixed solvent of o-dichlorobenzene/di-benzene (80/20 % by volume)

Sample concentration: 100 mg/1 milliliter solvent

Measurement temperature: 130°C

The pentad fraction of each sample was determined through measurement of split peaks attributed to a methyl group as measured in  $^{13}\text{C}$ -NMR spectrum. Signals in a peak attributed to a methyl group were assigned through a method disclosed in "Macromolecules 8,687, (1975)" by A. Zambelli et al.

(2) Crystal melting peak temperature ( $T_m$ ) of component (C)

$T_m$  was determined by the use of DSC-7 (product of Perkin-Elmer Co., Ltd.) in accordance with JIS K 7172. The method of determining  $T_m$  of component (B) will be described in the section "Production Example 1" below.

(3) Stress at 25% elongation

Strip samples (120 mm (machine direction)  $\times$  20 mm (transverse direction)) were cut out from each film, and stress (MPa) at 25% elongation of each sample was determined under stretching at a tensile rate of 200 mm/minute and a chuck distance of 40 mm.

(4) Storage modulus ( $E'$ ) and loss tangent ( $\tan\delta$ )

Storage modulus and loss tangent of each film were determined in the transverse direction by the use of a viscoelastic-meter DVA-200 (product of ITK Corp. Ltd.) under the following conditions: oscillation frequency of 10 Hz, temperature elevation rate of 3°C/minute, and measurement range of from -50°C to 150°C. The thus-obtained data were reduced to values at 20°C.

(5) Storage stability of feed material pellets

A feed material stored in a stock tank was suctioned by means of a blower through a hosepipe (inner diameter: 50 mm) equipped with a metal nozzle. Transfer failures of the material occurring during transfer to a measuring apparatus were evaluated on the basis of the following ratings:

AA...No problem

BB...Slightly unstable air transfer

CC...Blocking to impair transfer and measurement

DD...Completely solidified eventually.

(6) Wrapping machine adaptability

A tray made of foamed polystyrene (length: 200 mm, width: 150 mm, depth: 30 mm) was wrapped with a stretch film sample (width 350 mm) by the use of an automated wrapping machine (WminZERO1, product of ISHIDA). The wrapped tray was evaluated in terms of the properties shown in Table 2.

(7) Elastic recovery

The tray made of foamed polystyrene (length: 200 mm, width 150 mm, depth: 30 mm) employed in "(6) Wrapping machine adaptability" was wrapped in a manner similar to that of the foregoing term (6). The center of the wrap film covering the tray was indented by the use of a rod (diameter: 10 mm) having a hemispherical tip, at an indenting speed of 200 mm/minute, after which the rod was pulled away at the same speed. Indentation remaining one minute after the rod was pulled up was measured while the indentation depth was varied. The maximum indent depth at which an indentation was completely restored was derived, and evaluated on the basis of the following ratings:

(AA) > 25 mm,  $25 \text{ mm} \geq (\text{BB}) \geq 20 \text{ mm}$ ,  $20 \text{ mm} > (\text{CC}) \geq 15 \text{ mm}$ , and  $15 \text{ mm} > (\text{DD})$ .

(8) Transparency (Haze)

Haze of each film sample obtained was determined in accordance with ASTM D1003 by the use of a haze meter, and the haze value was evaluated on the basis of the following

ratings:

(AA) < 1.5%; 1.5% ≤ (BB) < 2.0%; 2.0% ≤ (CC) < 2.5%; and 2.5% ≤ (DD).

(9) High-temperature storage stability of film

A roll of each produced film was stored in a thermostatic room (50°C and RH of 60%) for 20 days, and unwinding characteristic was evaluated on the basis of the following ratings:

AA...No problem

BB...No problem in practice, but slightly heavy unwinding

CC...Heavy unwinding, problematic in practice

DD...Unwinding was impossible.

#### Production Example 1

(1) Preparation of catalyst and production of low-crystalline polypropylene

##### Synthesis of complex

Synthesis of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride

(1,2'-Dimethylsilylene)(2,1'-dimethylsilylene)-bis(indene) lithium salt (3.0 g, 6.97 mmol) placed in a Schlenk flask was dissolved in tetrahydrofuran (THF) (50 milliliter), and the solution was cooled down to -78°C. Iodomethyltrimethylsilane (2.1 milliliter, 14.2 mmol) was gradually added dropwise to the above solution, and the mixture was stirred at room temperature for 12 hours. The solvent was removed, and ether (50 milliliter) was added to



the solvent-removed mixture. The thus-formed liquid was washed with a saturated ammonium chloride solution. The organic phase was separated, and dried, followed by removing the solvent, to thereby yield 3.04 g (5.88 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindene) (yield: 84%).

Subsequently, the above-produced (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindene) (3.04 g (5.88 mmol)) and ether (50 milliliter) were placed in a Schlenk flask under nitrogen, and the mixture was cooled down to -78°C. n-BuLi (1.54 mol/liter hexane solution) (7.6 milliliter, 11.7 mmol) was added thereto, and the mixture was stirred at room temperature for 12 hours. The solvent was removed, and the formed solid was washed with hexane (40 milliliter), thereby yielding 3.06 g (5.07 mmol) of ether adduct of the target lithium salt (yield: 73%). The measurement results in accordance with  $^1\text{H-NMR}$  (90 MHz,  $\text{THF-d}_8$ ) were as follows:  $\delta$  0.04 (s, 18H, trimethylsilyl), 0.48 (s, 12H, dimethylsilylene), 1.10 (t, 6H, methyl), 2.59 (s, 4H, methylene), 3.38 (q, 4H, methylene), and 6.2 to 7.7 (m, 8H, Ar-H). The above-produced lithium salt was dissolved in toluene (50 milliliter) under nitrogen, and the solution was cooled down to -78°C. To the solution, a suspension of zirconium tetrachloride (1.2 g, 5.1 mmol) in toluene (20 milliliter), which had been cooled down to -78°C in advance, was added dropwise. After completion of addition, the

mixture was stirred at room temperature for six hours. The solvent of the reaction mixture was removed, and the thus-obtained residue was recrystallized from dichloromethane, to thereby yield 0.9 g (1.33 mmol) of (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride (yield: 26%). The measurement results in accordance with  $^1\text{H-NMR}$  (90 MHz,  $\text{CDCl}_3$ ) were as follows:  $\delta$  0.0 (s, 18H, trimethylsilyl), 1.02, 1.12 (s, 12H, dimethylsilylene), 2.51 (dd, 4H, methylene), and 7.1 to 7.6 (m, 8H, Ar-H).

#### Polymerization of propylene

To a reactor (made of stainless steel) having volume of 250 liter and equipped with a stirrer, n-heptane (37.4 L/h), triisobutylaluminum (product of Nippon Aluminum alkyls, Ltd., 19 mmol/h), methylaluminoxane (product of Albemarle, 13.6 mmol/h), and the above-obtained (1,2'-dimethylsilylene)(2,1'-dimethylsilylene)-bis(3-trimethylsilylmethylindenyl)zirconium dichloride (13.6  $\mu\text{mol/h}$ ) were continuously fed. Propylene and hydrogen were continuously fed to the reactor such that the ratio of hydrogen/propylene by volume in the gas phase was maintained at 0.05, and the total pressure in the reactor was maintained at 0.8 MPaG. Polymerization was continuously performed at the temperature of 60°C for a residence time of 90 minutes, thereby forming low-crystalline polypropylene.

#### Post treatment

To the thus-produced polymerization solution, a phenol-

type antioxidant (Irganox 1010, product of Ciba Specialty Chemicals) (500 ppm based on polymer) and a phosphorus-type antioxidant (Irgafos 108, product of Ciba Specialty Chemicals) (1,000 ppm based on polymer) were added. The mixture was subjected to melt flushing by the use of two stages of flush drums equipped with a plate-fin-type polymer heater at a jacket temperature of 220°C, thereby removing solvent.

## (2) Production of granules

After completion of flushing, the molten resin (resin temperature: 200°C) was extruded by the use of a gear pump and granulated by the use of a rotatable-drum-type submerged cutter equipped with a liquid-solid separator (Type PASC-21-HS, product of Tanabe Plastics Machinery Co., Ltd.). The time for transferring resin chips formed through cutting to the solid-liquid separator (residence time of granules in water) was predetermined by modifying the length of a connection tube connecting the submerge cutter and the solid-liquid separator. In the production of granules, the residence time of granules in water was regulated to 4 sec, and the water temperature was 20°C. Through the above procedure, low-crystalline polypropylene granules were obtained.

The low-crystalline polypropylene granules were found to have a [mmmm] of 0.45, a [rrrr] of 0.024, a [rrrr/(1-mmmm)] of 0.044, an MFR of 7.3 g/10 minutes, and T<sub>m</sub> of 81°C.

The T<sub>m</sub> was determined through the following procedure.

By the use of a differential scanning calorimeter (DSC-7, product of Perkin Elmer Co., Ltd.), a sample (10 mg) was melted at 230°C for three minutes under the atmosphere of nitrogen. The melt was then cooled down to -40°C at a cooling rate of 1°C/minute, maintained at -40°C for three minutes, and heated at a temperature elevation rate of 10°C/minute, thereby obtaining an endothermic curve attributed to melting of the resin. The temperature corresponds to the maximum peak top was determined as a melting point ( $T_m$ ).

<Example 1>

Component (B)

Soft polypropylene resin having controlled stereoregularity (low-crystalline polypropylene granules produced in Production Example 1, hereinafter abbreviated as "FPP"): 50 % by weight

Component (C)

Propylene-ethylene random copolymer (ethylene unit content: 4 % by mole, MFR = 1.3 g/10 minutes, and  $T_m$  = 147°C; hereinafter abbreviated as "RPP"): 30 % by weight

Component (D)

Hydrogenated petroleum resin (Arkon P125, product of Arakawa Chemical Industries, Ltd., softening point: 125°C; hereinafter abbreviated as "hydrogenated petroleum resin"): 20 % by weight

The mixed resin composition containing the above three

component was formed to an intermediate layer (thickness 8.8  $\mu\text{m}$ ). EVA (vinyl acetate unit content: 15 % by weight, MFR = 2.0 g/10 minutes at 190°C under a load of 21.18 N) serving as component (A) (100 parts by weight) and diglycerin oleate ester (3.0 parts by weight) serving as an anti-clouding agent were melt kneaded to produce a composition, and two surface layers (1.6  $\mu\text{m}$ ) were formed from the composition. The laminated film having a total thickness of 12  $\mu\text{m}$  (1.6  $\mu\text{m}$ /8.8  $\mu\text{m}$ /1.6  $\mu\text{m}$ ) was formed through co-extrusion inflation molding at a three-layer ring die temperature of 190°C and a blow-up ratio of 6.0.

#### <Example 2>

The procedure of Example 1 was repeated, except that the proportions of the three resins employed in Example 1 for producing the intermediate layer were altered to the following proportions:

component (B):	55 % by weight
component (C):	35 % by weight
component (D):	10 % by weight, to thereby produce a

laminated film having a total thickness of 12  $\mu\text{m}$  (1.6  $\mu\text{m}$ /8.8  $\mu\text{m}$ /1.6  $\mu\text{m}$ ).

#### <Comparative Example 1>

The procedure of Example 1 was repeated, except that the proportions of the three resins employed in Example 1 for producing the intermediate layer were altered to the

following proportions:

component (B): 70 % by weight  
component (C): 30 % by weight  
component (D): 0 % by weight, to thereby produce a  
laminated film having a total thickness of 12  $\mu\text{m}$  (1.6  $\mu\text{m}$ /8.8  
 $\mu\text{m}$ /1.6  $\mu\text{m}$ ).

<Comparative Example 2>

The procedure of Example 1 was repeated, except that a soft polypropylene resin having controlled stereoregularity (REX flexfpo W110, product of Huntsman Polymer Corporation, hereinafter abbreviated as "FPO," propylene unit content: 100 % by mole, [mmmm] = 0.445, [rrrr] = 0.123, a [rrrr/(1-mmmm)] = 0.222, MFR = 6 g/10 minutes, and  $T_m = 158^\circ\text{C}$ ) was used instead of component (B) employed in Example 1 for producing the intermediate layer, to thereby produce a laminated film having a total thickness of 12  $\mu\text{m}$  (1.6  $\mu\text{m}$ /8.8  $\mu\text{m}$ /1.6  $\mu\text{m}$ ).

<Comparative Example 3>

The procedure of Example 1 was repeated, except that the proportions of the three resins employed in Example 1 for producing the intermediate layer were altered to the following proportions:

component (B): 35 % by weight  
component (C): 30 % by weight  
component (D): 35 % by weight, to thereby produce a

laminated film having a total thickness of 12  $\mu\text{m}$  (1.6  $\mu\text{m}$ /8.8  $\mu\text{m}$ /1.6  $\mu\text{m}$ ).

<Comparative Example 4>

Commercial poly(vinyl chloride) stretch film (thickness: 15  $\mu\text{m}$ , hereinafter abbreviated as "PVC") was similarly evaluated.

Characteristics and performance of the above film samples evaluated as described above are shown in Table 1.

Table 1

Intermediate layer composition (parts by wt.)		Example		Comparative Example			
		1	2	1	2	3	4
FPP		50	55	70		35	PVC
FPO					50		
RPP		30	35	30	30	30	
Hydrogenated petroleum resin		20	10		20	35	
Stress at 25% elongation (MPa)	M direction	7.65	7.65	7.36	10.79	6.37	11.77
	T direction	5.88	6.08	5.88	7.36	4.41	5.88
Storage modulus (E') ( $\times 10^8$ Pa)		2.5	1.7	1.5	2.8	1.5	1.9
Loss tangent (tan $\delta$ ) (-)		0.33	0.3	0.12	0.25	0.3	0.35
Feed material pellets storage stability		AA	AA	AA	CC	AA	-
Wrapping machine adaptability							
Cut property		AA	BB	CC	AA	AA	AA
Wrinkle at wrapping		AA	AA	CC	BB	CC	BB
Bottom sealing property	Performance of wrapping the bottom	AA	BB	DD	BB	BB	AA
	Heat sealability	AA	AA	AA	AA	CC	-
Break resistance		BB	AA	AA	BB	CC	AA
Elastic recovery (maximum indentation depth)		BB 22 mm	BB 23 mm	BB 25 mm	CC 18 mm	CC 16 mm	AA 28 mm
Transparency (Haze) (%)		AA 1.2	AA 1.2	AA 1.0	BB 1.8	AA 1.3	AA 1.0
High-temp. storage stability		AA	AA	AA	BB	DD	-
Overall evaluation		BB	BB	DD	CC	DD	BB



Table 2

Evaluated properties	AA	BB	CC	DD
Cut property	Being cut without problem	Unsatisfactory cut edge, but employable	Difficult to be cut, with transfer failure	Impossible to be cut
Wrinkle at wrapping	No wrinkle generated under normal conditions	Wrinkles generated to slight extent, but employable	Wrinkle generation $\geq 30\%$ film surface, not restored	Wrinkle generation over almost entire film surface
Bottom sealing property	Perform-ance of folding the bottom	Beautifully folded, no stiffness or detachment	Wrinkle generated, nearly detached	Impossible to fold the film, causing lumps
	Heat seal-ability	Partially melt-adhered firmly, but employable	Holes formed at higher temperature, and poor melt-adhesion at lower temperature	Impossible of melt-adhesion
Tear resistance	No tearing	Occasionally tearing under high tension	Occurrence of tearing $\geq 10\%$	Occurrence of tearing $\geq 50\%$

As is clear from Table 1, a laminated film comprising at least three layers including an intermediate layer formed of a resin layer containing a polypropylene resin having controlled stereoregularity as stipulated in the present invention, a crystalline polypropylene resin, and a petroleum resin; and two surface layers containing, as a main component, an ethylene polymer successfully provides a vinyl-chloride-free stretch film which has excellent characteristics such as wrapping efficiency, wrapping finish, elastic recovery, bottom sealing property, and transparency, as well as has high long-term film stability (Examples 1 and 2). In contrast, in Comparative Example 1 where the intermediate layer contains no petroleum resin, performance of folding the bottom, among wrapping machine adaptabilities, is poor. The film of Comparative Example 2 employs a soft polypropylene resin having controlled stereoregularity. However, when the relation between the meso pentad fraction  $[mmmm]$  and the racemic pentad  $[rrrr]$  (i.e.,  $[rrrr/(1-mmmm)]$ ) is in excess of 0.1, storage stability of feed material pellets is insufficient, and elastic recovery of the wrap film of packaged products is unsatisfactory as compared with poly(vinyl chloride) film. The film of Comparative Example 3 contains petroleum resin in an amount (parts) in excess of the range stipulated in the present invention. In this case, the produced film exhibits poor storage stability at high temperature, and other properties such as tear resistance are insufficient.

### Industrial Applicability

According to the present invention, a chlorine-free stretch film which is excellent in storage stability of feed material pellets, wrapping efficiency, wrapping finish, elastic recovery, bottom sealing property, transparency, etc. and has favorable long-term stability and economic merits can be provided.